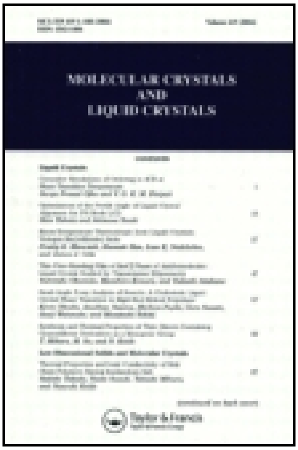

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Toshio Kawasaki , Toshihide Kamata , Hirobumi Ushijima , Shigeo Murata , Fujio Mizukami , Yuki Fujii & Yoshiharu Usui (1996): Luminescence of Schiff Bases in Solid State, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 257-262

To link to this article: http://dx.doi.org/10.1080/10587259608042295

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 257–262
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LUMINESCENCE OF SCHIFF BASES IN SOLID STATE

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Abstract We prepared a series of schiff base compounds and investigated luminescence spectra of these compounds in the solid state. The schiff base compounds composed of phenyl rings with a hydroxyl group at an ortho position, imino groups and a butane or octane bridge show very strong luminescence in the solid state. For example, Msalbn (**19**) obtained from 2-hydroxy-acetophenone and 1,4-diaminobutane (excitation wavelength = 396 nm, emission wavelength = 496 nm, relative intensity = 38.02) and *p*-Me-anil (**21**) obtained from salicylaldehyde and *p*-toluidine (excitation wavelength = 396 nm, emission wavelength = 545.5 nm, relative intensity = 33.79) showed the strongest intensities in the luminescence. It was expected that luminescence properties of the compounds in the solid state were affected by molecular structure, intermolecular interaction and a type of the aggregation of molecules.

INTRODUCTION

Various solid luminous substances have been synthesized for luminescent lamp, Braun tube, etc. Most of the solid luminous substances are inorganic compounds taking certain polymers structure, for example, zinc sulfide, zinc oxide, magnesium tungstate, etc. However, it is quite rare for small molecules such as metal complexes and organic compounds, which can be easily vaporized or sublimed, to emit stably luminescence in solid state.

As regarding small molecules, the investigations on the luminescence properties have been so far limited to fused polycyclic hydrocarbons such as anthracence, terphenyl, etc. As far schiff bases and their metal complexes, the photochromism and thermochromism have been investigated in detail for compounds consisting of a carbonyl compound and a monoamine in both the solid and liquid states.[1, 2, 3, 4, 5] However, the luminescence properties of the compounds in solid state have not been investigated enough, for example the relative intensities between the compounds, although fluolescence spectra of N-(4-chloro-salicylidene)aniline, N-(salicylidene)-2-aminopyridine and N-(salicyli-dene)-3-aminopyridine in the solid state have been reported.[4]

On the process of the investigation on the third order nonlinear optical properties of the schiff base metal complexes, we found that certain schiff bases composed of a carbonyl compound and a diamine show strong luminescence in solid state. So we prepared a series of schiff base compounds and investigated the relationship between the molecular structures and the luminescence properties in the solid state.

EXPERIMENTAL

Preparation of Schiff Bases

Schiff bases were prepared in the usual method.[6, 7, 8] Two types of schiff base compounds (diamine/carbonyl = 1/2, monoamine/carbonyl = 1/1) were synthesized by stirring stoichiometric amounts of an appropriate carbonyl compound and an amine in ethanol solution. The compounds were purified by repeating the recrystallization from the ethanol. Chemical structures of schiff base compounds are shown in FIGURE 1.

Measurement of Luminescence Spectra

Schiff base compounds in powdery crystalline form were interposed between two slide glasses. Their luminescence spectra were recorded on a HITACHI Model 850 fluorescence spectrophotometer at room temperature. First of all, the tentative maximum emission wavelength (λ_f) which showed the strongest intensity was tentatively searched by scanning the emission wavelength from 400 to 700 nm under the irradiation of 350 nm light. Next, the maximum excitation wavelength (λ_{EX}) which gave tentative λ_f with the strongest intensity was found by scanning the excitation wavelength from 250 to 500 nm. Furthermore, under the irradiation of the light with λ_{EX} obtained in the above manner, the real maximum luminescence wavelength and intensity were determined.

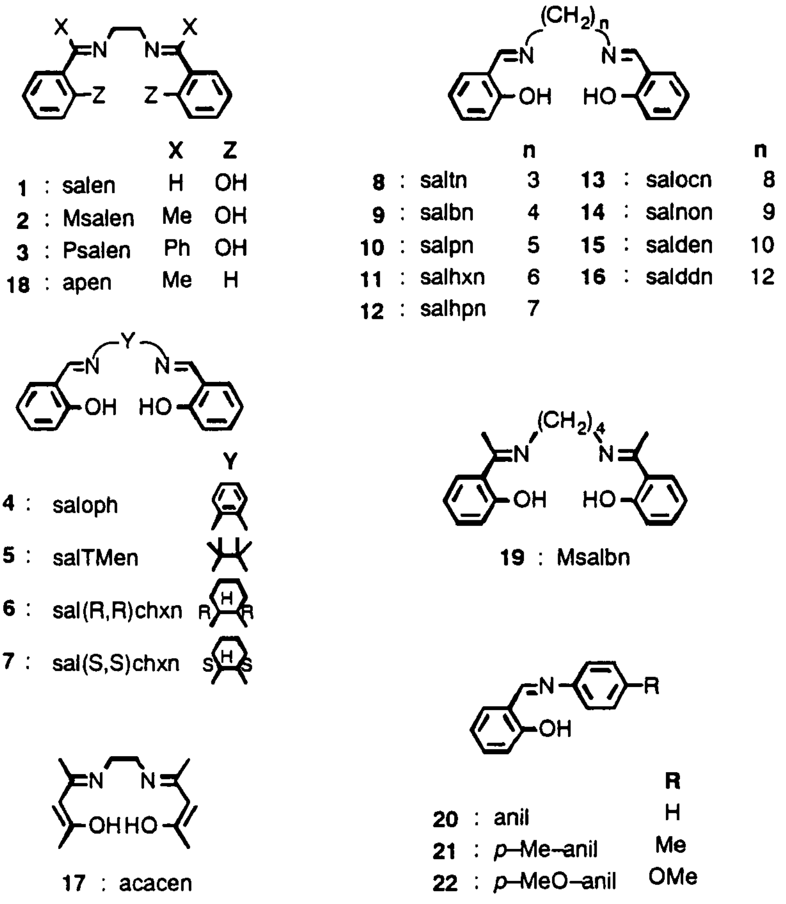

FIGURE 1 Molecular structures of schiff base compounds.

RESULTS AND DISCUSSION

To evaluate the luminescence properties, firsts of all, thin films of the compounds were made on quartz substrates using evaporation technique. The thin films were transparent just after the preparation, but became opaque by phase transition soon. When the films were transparent, they showed no luminescence. On the contrary, the opaque films after the phase transition showed luminescence. This suggests that how the schiff base molecules associate and aggregate in the solid state is very important for the luminescence. Also, from these results, the luminescence spectra of the schiff bases were then measured by interposing their powdery crystals between two slide glasses.

In order to check the effect of crystal grain size on the luminescence spectrum, the luminescence spectra of salen (**1**) whose crystals were different in grain size were compared. But, all the spectra were basically identical and it was difficult to recognize the difference in crystal size between the spectra.

TABLE I is the luminescence properties of schiff base compounds (**1**~**22**). Most of the schiff base compounds prepared here show their maximum excitation wavelengths at around 395 nm, and their luminescence maxima appear at about 500 nm.

TABLE I Value of emission wavelength of schiff base compounds.

Sample	λ_{EX}^{a} / nm	λ_{f}^{b} / nm	Relative Intensity^{c}
1	394.5	502	1.00
2	396	494	23.91
3	420	530	0.51
4	430	560	10.67
5	395	509.5	0.84
6	395.5	500	0.13
7	418	510	0.46
8	451	498	0.34
9	396	495.5	16.81
10	395	497	11.30
11	466	503	0.22
12	390	498	0.98
13	397	497	12.34
14	339	496	3.28
15	395	496	11.15
16	395	495	8.50
17	451	521.5	0.39
18	350	515	0.30
19	395.5	487	38.02
20^{d}	–	–	–
21	396	545.5	33.79
22	360	531	0.48

a : maximum excitation wavelength, b : maximum emission wavelength,
c : luminescence intensity was measured at maximal luminescence wavelength. intensity compared with salen(1), d : 20 is photpchromism.

Samples **1** to **3** show the effect of the substituents on α-position of imino group (>C=N–) on the spectra. When the substitute group was methyl group, the highest intensity was obtained (Msalen **2**, FIGURE 2).

Sample **4** to **16** show the effect of the structure and length of diamine bridge on luminescence spectra. When the bridging groups were phenylene, butylene, pentylene, octylene and decylene, higher intensities were obtained with saloph (**4**), salbn (**9**), salpn (**10**), salocn (**13**) and salden (**15**) (FIGURE 3).

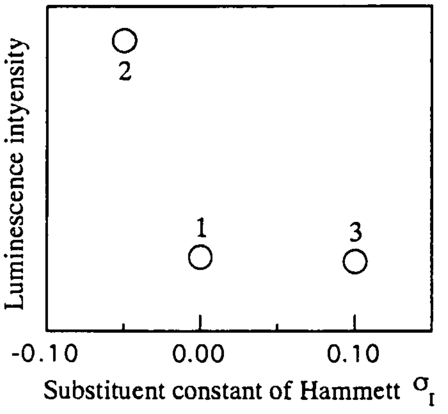

FIGURE 2 Correlation of luminescence intensities with Hammet's substituent constants.

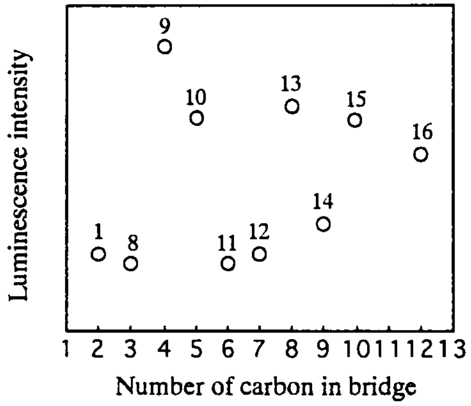

FIGURE 3 Effect of bridge's length.

In the comparison of acacen (**17**) and **1**, the intensity of **17** is smaller than that of **1**. From the comparison of apen (**18**) and **2**, it is found that **18** shows much smaller intensity than that of **2**. These indicate that a phenyl ring or aromaticity of a carbonyl compound and a hydroxyl group at the ortho position on the phenyl ring are essential for the schiff base compounds to show strong luminescence in the solid state.

From the above results, it is expected that a schiff base compound composed of phenyl rings with a hydroxyl group at the ortho position, imino group and a butane or octane bridge shows very strong luminescence in the solid state. So, the compound having those functional groups, Msalbn (**19**) was prepared. This compound showed very strong luminescence as was expected, and the intensity was the strongest in this work (excitation wavelength = 396 nm, emission wavelength = 496 nm, relative intensity = 38.02).

Furthermore, we tried to apply the above empirical rules of the substituent effect on the luminescence for a system of schiff bases obtained from a carbonyl compound and a monoamine, and prepared the samples, anil (**20**), *p*-Me-anil (**21**) and *p*-MeO-anil (**22**). As the results, we newly found that **21** also shows very strong luminescence in the solid state.

CONCLUSION

The schiff base compounds composed of phenyl rings with a hydroxyl group at a ortho position, imino groups and a butane or octane bridge show very strong luminescence in the solid state. For example, Msalbn (**19**) obtained from 2-hydroxy-acetophenone and 1,4-diaminobutane (excitation wavelength = 396 nm, emission wavelength = 496 nm, relative intensity = 38.02) and *p*-Me-anil (**21**) obtained from salicylaldehyde and *p*-toluidine (excitation wavelength = 396 nm, emission wavelength = 545.5 nm, relative intensity = 33.79) showed the strongest luminescence in the solid state. It was expected that luminescence properties of the compounds in the solid state were affected by molecular structure, intermolecular interaction and a type of the aggregation of molecules.

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